# Limnology

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# Robert G. Wetzel

Michigan State University



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# CHAPTER FIVE

Solar radiation is of fundamental importance to the entire dynamics of freshwater ecosystems. Almost all energy that controls the metabolism of lakes is derived directly from the solar energy utilized in photosynthesis, either autochthonously (within the lake) or allochthonously (within the catchment basin and brought to the lake in various forms of organic matter). The utilization of this energy received by the lake and from its drainage basin, and factors that influence the lake's efficiency of conversion of solar energy into potential chemical energy, are basic to lake productivity.

In addition to these effects, the absorption of solar energy and its dissipation as heat have profound effects on the thermal structure, water mass stratification, and circulation patterns of lakes. The array of attendant effects on nutrient cycling, distribution of dissolved gases and biota, and behavioral adaptations of organisms exert major controls on the environmental milieu. Therefore, the optical properties of lakes and reservoirs are important regulatory parameters in the physiology and behavior of aquatic organisms. They deserve detailed scrutiny.

LIGHT AS AN ENTITY

The term *light* is often confusing, in part because of different usages in absolute physical terms, reactions of visual receptors to light, and responses of plants to light energy. For the purposes of this discussion, it is essential that it be viewed physically, as part of the radiant energy of the electromagnetic spectrum. Light is energy, that is, something that is capable of doing work and of being transformed from one form into another, but it can neither be created nor destroyed. Radiant energy is transformed into potential energy by biochemical reactions, such as photosynthesis, or to heat. Energy transformations are far from 100 per cent efficient in a system such as a lake, and most of the radiant energy is lost as heat.

#### **ELECTROMAGNETIC SPECTRUM**

The electromagnetic spectrum is expressed as units of frequency and wavelength. At one extreme are cosmic rays of very high frequency ( $10^{24}$  cps) and short wavelength ( $10^{-14}$  cm), and at the other are radio and power transmission waves of low frequency (1 cps) and long wavelength (to  $10^{10}$  cm). For all practical purposes, solar radiation constitutes all of the significant energy input to aquatic systems. This solar flux of energy

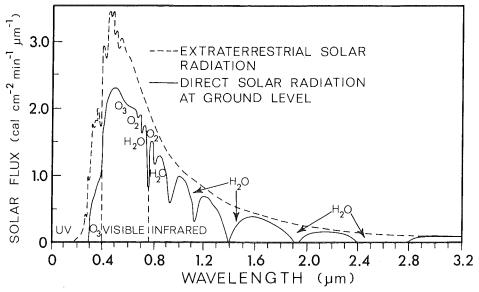


Figure 5-1 Extraterrestrial solar flux and that at the surface of the earth showing major absorption bands from atmospheric  $O_2$ ,  $O_3$ , and water vapor. (Modified from Gates, 1962.)

consists of wavelengths of 100 to >3,000 nm (1000 to >30,000 Å), from the ultraviolet (UV) to infrared radiation, as it is received extraterrestrially (Fig. 5–1). As solar radiation penetrates and diffuses in the atmosphere of the earth, the energy of certain wavelengths is strongly absorbed and attenuated by scattering. The visible portion of the spectrum, with maximum energy flux in the blue and green portions (480 nm) of the visible range, is only a small amount of the total energy radiated by the sun (Fig. 5–1). Ultraviolet energy is strongly absorbed by ozone and oxygen, and infrared wavelengths are absorbed by water vapor, ozone, and carbon dioxide.

With respect to the mechanisms by which life receives light energy, it is important to view light as the radiation of packets of energy termed quanta or photons. A photon is a pulse of electromagnetic energy; as this energy propagates it has an electric (E) and magnetic (H) field, with respect to direction of flux and wave characteristics of wavelengths ( $\lambda$ ) and amplitude (A) (Fig. 5–2). Hence, light is effectively a transverse wave of energy that behaves as a movement of particles with defined mass. The photon carries energy in a wave conformation.

#### ABSORPTION OF LIGHT

Absorption of light by atoms and molecules can occur when the electrons of the atoms and molecules resonate at frequencies that correspond to a photon's energy state. In the collision of an electron and a photon, the electron gains the quantum of energy lost by the photon. It is important to keep this basic photochemical relationship in mind, since the quantum energy imparted by the photon functions in relation to frequency, and each molecular or atomic species has a unique set of absorption characteristics or bands. Life responds to quantum energy of photons at specific frequencies.

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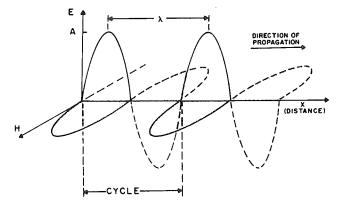
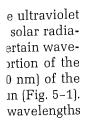


Figure 5-2 Instantaneous electric (E) and magnetic (H) field strength vectors of a light wave as a function of position along the axis of propagation (x), showing the amplitude (A), wavelength (\(\)), cycle, and direction of propagation. (From Bickford, E. D., and Dunn, S.: Lighting for Plant Growth. Kent, Ohio, Kent State University Press, 1972.)

If the energy distribution of solar flux is plotted against wavelength, as was done in Figure 5–1, the maximum monochromatic intensity of sunlight appears to occur in the blue-green portion of the visible spectrum, an illusion caused by the manner of presenting the data. It is more meaningful to express energy against frequency, where the area under any portion of the curve is directly proportional to energy (Fig. 5–3). The



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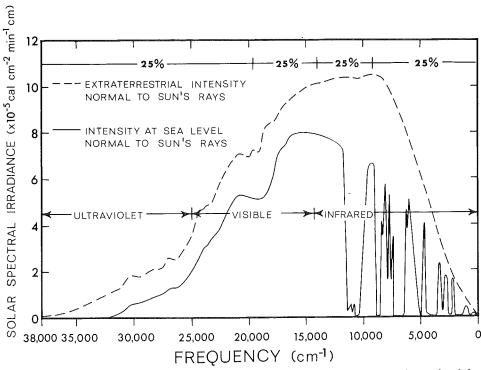


Figure 5-3 Solar spectrum at the mean solar distance from the earth as received outside of the earth's atmosphere and at sea level on a surface perpendicular to the solar rays (solar constant of 2.00 cal cm<sup>-2</sup> min<sup>-1</sup>). (Modified from Gates, 1962.) Frequency (cm<sup>-1</sup>) of the abscissa refers to the wavenumber (v¹), or number of wavelengths per cm, and is therefore equal to the reciprocal of the wavelength.

TABLE 5-1 Speed of Light (589 nm, Sodium D-lines)

MEDIUM	SPEED (cm sec <sup>-1</sup> )		
Vacuum Air (760 nm, 0°C) Water Glass	$2.9979 \times 10^{10}$ $2.9972 \times 10^{10}$ $2.2492 \times 10^{10}$ $1.9822 \times 10^{10}$		

energy of the photon in the electromagnetic spectrum is proportional to frequency and inversely proportional to wavelength in accordance with Planck's Law:

$$\epsilon = hv$$

where:

 $\epsilon$  = energy of the photon, ergs

h = Planck's constant,  $6.63 \cdot 10^{-27}$  erg-seconds

v =frequency of the radiation in cycles per second.

When energy is expressed against frequency (Fig. 5-3), the true maximum energy of solar irradiance is found in the infrared at wavelengths somewhat greater than 1000 nm or  $1\mu$ m. The median value of irradiance occurs in the near infrared at a frequency of 14,085 cm<sup>-1</sup> (= a wavelength of 710 nm), slightly above the visible range. A major portion (29 per cent) of the incoming radiation occurs at wavelengths greater than 1,000 nm (frequency <10,000 cm<sup>-1</sup>) and 50 per cent beyond the red portion of the visible range. This distribution of energy shifts somewhat as the solar radiation passes through the earth's atmosphere (Fig. 5-3). The point to be made, however, is that a large portion of irradiance impinging on the surface of a lake is in the infrared portion of the solar spectrum and has major thermal effects on the aquatic system.

Wavelength ( $\lambda$ ) is a quantitative parameter of any periodic wave motion, not only of light but also of water movements, as will be discussed later on. It is defined simply as the linear distance between adjacent crests of waves, and is equal in cm to the speed of light ( $c = 2.998 \times 10^{10}$  cm sec<sup>-1</sup>) divided by the frequency (v) in cycles per second (cps):

$$\lambda = c/v$$

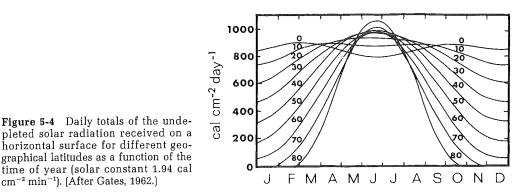
Wavelength is also often expressed as the wave number  $(v^1)$  [or k], which is the number of wavelengths per cm, or the reciprocal of the wavelength:

$$v^1 = 1/\lambda$$

The speed of light is reduced in a roughly linear fashion as it passes through transparent materials of increasing density (Table 5–1). (A conversion table for commonly used units of length and irradiance is given in the Appendix.)

# Light Impinging on Lakes

The amount of solar energy that reaches the surface of a lake is dependent upon an array of dynamic factors. The amount of direct solar energy per unit of time from



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the sun, incident upon a surface outside the atmosphere perpendicular (normal) to the rays of the sun at an average distance of the earth from the sun, is referred to as the solar constant.\* The amount of energy received is a function of the angular height of the sun incident to the earth and is greatly influenced by latitude and season (Fig. 5-4). The angle of light rays impinging on the water has a marked effect upon the productivity of lakes, as will be illustrated repeatedly in subsequent chapters. In equatorial regions, sunlight impinges vertically and leads to relatively constant energy inputs. This contrasts strongly with temperate and polar areas, where the sun's angle changes with the sequence of the seasons. The time of day is another factor that strongly influences the solar flux reaching the surface of a lake, for time of day influences the position of the sun and the distance of the path the light must travel through the absorbing atmosphere. In the polar extremes, for example, direct solar energy decreases to zero for over one-third of the year, and polar waters then receive thermal radiation only from indirect sources.

cm<sup>-2</sup> min<sup>-1</sup>). (After Gates, 1962.)

The absorptive capacities of the atmosphere for solar radiation are governed largely by oxygen, ozone, carbon dioxide, and water vapor, as discussed previously. Additionally, atmospheric transparency can be strongly modified in some regions by both industrial- and urban-derived contaminants. Scattering and absorption also increase in moist air, which is more common on the downwind side of large water bodies. The elevation of a lake and the angular height of the sun both determine the quantity of atmosphere through which the radiation must travel. In sum, the amount and spectral composition of direct solar radiation reaching the surface of a water body vary markedly with latitude, season, time of day, altitude, and meteorological conditions.

Indirect solar radiation from the sky is largely the result of scattering of light as it passes through the atmosphere. The extent of scattering is a function of the fourth power of the frequency, and therefore the UV and shorter wavelength radiation of high frequency is reduced by about one-fourth as a result of scattering. The result is the blue sky we see directly overhead on clear days. The factors influencing direct solar radia-

<sup>\*</sup>The solar constant is difficult to measure but recent evidence from satellite instrumentation indicates a value of 1.94 cal cm<sup>-2</sup> min<sup>-1</sup> (Drummond, 1971; Gates, personal communication); Hickey, et al. (1980) found 1.97 cal cm<sup>-2</sup> min<sup>-1</sup> (1376.0 W m<sup>-2</sup>).

tion also influence scattering, but of particular importance are solar height and the atmospheric distance through which the light must pass. The percentage of indirect radiation increases significantly as deviations of the rays from the perpendicular increase, e.g., 20 to 40 per cent at a sun elevation from the horizontal of 10°, in contrast to 8 to 20 per cent at a sun elevation of 40°.

#### DISTRIBUTION OF RADIATION IMPINGING ON LAKES

Solar radiation that impinges upon the surface of an inland water body does not all penetrate the water. A significant portion is *reflected* from the surface, and is lost from the system unless it returns to the lake after being backscattered from the atmosphere or surrounding topography.

The extent of reflectivity of solar radiation varies greatly with the angle of incidence, the surface characteristics of the water, the surrounding topography, and the meteorological conditions. The reflection (R) of unpolarized direct sunlight as a fraction of the incident light is a function of Fresnel's law:

$$R = \frac{1}{2} \left[ \frac{\sin^2{(i-r)}}{\sin^2{(i+r)}} + \frac{\tan^2{(i-r)}}{\tan^2{(i+r)}} \right]$$

where i = angle of incidence, and r = angle of refraction. This function states simply that the reflectivity is dependent upon the solar height from the zenith (Fig. 5-5A), i.e., the greater the departure of the angle of the sun from the perpendicular, the greater the reflection will be. Indirect radiation from the sky is also reflected from a water surface, but is less affected by solar height (Fig. 5-5B). Under an overcast sky the

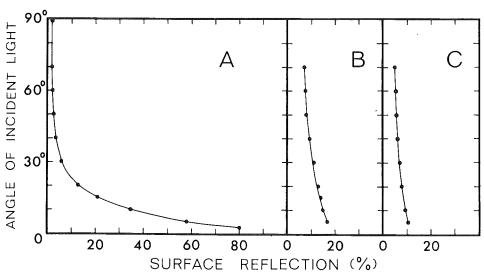


Figure 5-5 Surface reflection and backscattering as a percentage of total solar radiation at angles of incidence varying from the horizontal. A, clear, cloudless conditions; B, reflection of diffuse light under moderate cloud cover; C, heavily overcast conditions. (Generated from data in Steleanu, 1961, and from Sauberer, 1962.)

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amount of indirect light that is reflected decreases (Fig. 5-5C). An average reflectance loss value of 6.5 per cent is common, although reflective losses can be reduced further if surrounding topography, mountains for example, moderates low-angle radiation (Sauberer, 1962).

When the surface of the water is disturbed by wave action, reflection increases by about 20 per cent at low angles of incident light (approximately 5°) to approximately a 10 per cent increase at higher angles (5 to 15°). The difference is small at angles of incidence at greater than 15° from the horizontal. Reflection may decrease slightly when the waves are very large and the light is exposed to the water surfaces at angles more closely approaching the perpendicular. Ice and especially snow cover markedly affect the reflectivity of light from the surfaces of lakes. Although data are very meager, clear, smooth ice acts with reflection characteristics similar to those of the undisturbed liquid phase. Changes in texture of the ice generally result in increases in reflectivity. Reflection increases markedly with the greatly increased angles and quantity of surface planes of granular ice in the form of snow cover. On the average, about 75 per cent of incident light striking snow is reflected, and under some conditions, the amount reflected can be as high as 95 per cent.

Of the total incident light impinging upon the surface of a lake, a reasonable average amount that is reflected on a clear, summer day is 5 to 6 per cent. This mean value increases to about 10 per cent during winter. Qualitatively, light in the red portion of the spectrum is reflected to a slightly greater extent than light of higher frequencies, particularly at low angles of incidence. About one-half of the total quantity of light leaving the lake is by reflection, and half by scattering of light.

#### **SCATTERING**

Scattering of light from the water results in the loss of large amounts of light energy from the lake. This phenomenon is apparent to anyone who has looked down into relatively clear waters where the surface reflection is eliminated. Of the total light energy entering the water, portions are absorbed by the water and its suspensoids, as will be discussed in detail further on, and a significant portion is scattered. The scattering of light is the result of deflection of quanta by the molecular components of the water and its solutes but also, to a large extent, by particulate materials suspended in the water.

The scattering of light energy can be viewed in a simple way as a composite of reflection at a massive array of angles internally within the lake. The energy scattered in all directions within a volume of water varies greatly with the quantity of suspended particulate matter and its optical properties. Volcanic siliceous materials, for example, scatter light much less than suspended particulate matter of lower transparency.

Scattering of light can change significantly with depth, season, and location in the lake and in response to variations in the distribution of particulate matter. When particulate matter is concentrated in the middle zone of great density change (metalimnion) of a thermally stratified lake, either as a result of reduced rates of sinking as the particles encounter increased water densities, or as a result of the development of large populations of plankton in certain strata, scattering of light can increase. Scattering can also increase markedly in areas of the lake where wind-induced currents and wave action agitate and temporarily suspend littoral and shore deposits of particulate matter

(Tyler, 1961b). When dimictic or amictic lakes (see next chapter) undergo complete circulation, a significant portion of the recent sediments of the lake basin are brought into resuspension (Davis, 1973; Wetzel, et al., 1972; White and Wetzel, 1975) and can affect the scattering properties of the lake for an extensive period (weeks). Similarly, the variable influxes of suspended inorganic and organic matter from stream inflows to reservoirs can radically increase the scattering of light nonuniformly within the lake basin. These alterations can be short- or long-lived depending upon the composition and density of the material and the density characteristics of the recipient water at that particular time.

A significant amount of light can be reflected and scattered from the sediments both in the littoral zone and in the shallow areas of the lake, as well as from the bottom of moderately deep, clear lakes (Fig. 5–6). The amount of light returned to the water is dependent upon the composition of the sediments; sand sediments or those sediments rich in CaCO<sub>3</sub> (calcium carbonate, marl) reflect considerably more light than dark-colored sediments of high organic content.

Differential scattering of light also depends on scattering coefficients for different wavelengths, as well as on absorption characteristics for different wavelengths. In very clear water, scattering occurs predominantly in the blue portion of the visible spectrum. As the quantity and size of suspensoids increase, radiation of longer wavelengths is scattered preferentially and greater absorption of the light of high frequencies occurs. Hard-water lakes with large amounts of suspended CaCO<sub>3</sub> particles characteristically backscatter light that is predominantly blue-green; lakes rich in suspended organic materials appear more green or yellow.

The diffuse light from scattering and reflecting sources is of obvious importance to organisms that utilize it directly in photosynthesis or indirectly in behavioral responses. In lake systems where light enters the environment unidirectionally from above, diffuse light can form a major supplementary source of energy. The amount of light scat-

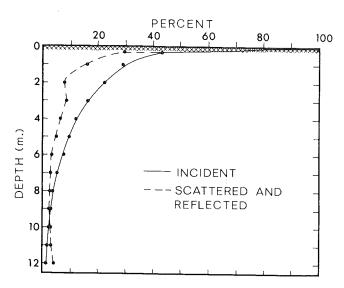


Figure 5-6 Comparison of incident light penetration (per cent of total surface light) with depth to that backscattered from concentrations of plankton, especially at 3 m, and from calcareous sediments. Lawrence Lake, Michigan; 17 March 1972; 23 cm cloudy ice.

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tering can easily be one-fourth of that light absorbed by the water. The values are likely to be even higher, since most of the existing data on scattering are based on unidirectional  $(2\pi-\text{flat})$  instruments. When values using this type of sensor are compared with those obtained with instruments approaching  $4\pi$  (spherical) geometry (e.g., Rich and Wetzel, 1969), higher values are commonly found. A portion of the scattered light is returned to the surface of the lake, and much (80 to 90 per cent) of that which returns to the surface is lost to the atmosphere. Because of differences in light-wave refraction properties at different frequencies, somewhat less of the red scattered light reaches the surface than the blue.

Several terms are in common usage in relation to light radiation used by photosynthetic organisms. Photosynthetically active radiation (PAR) is defined as radiation in the 400-700-nm waveband. The photosynthetically active range may extend below 400 nm to wavelengths as low as 290 nm (Halldal, 1967; Klein, 1978), but the amount of subsurface irradiance available at the shortest wavelengths is very small, especially if the water contains significant amounts of dissolved organic compounds (as most lakes do; see following discussion). PAR is a general radiation term that is applicable to both energy terms and the preferred photon (quantum) terms.

Photosynthetic irradiance is the radiant energy (400 to 700 nm) incident per unit time on a unit surface (i.e., radiant energy flux density of PAR in units such as watts m<sup>-2</sup>). Photosynthetic photon flux density is the number of photons (quanta) in the 400-700-nm waveband incident per unit time on a unit surface (i.e., photon flux density

of PAR in units in µeinsteins second-1 m-2).\*

Total underwater light received by a receptor system, such as that received by an algal cell from all angles, is the optimum measure of radiant energy available for photosynthesis. This realistic value is the photosynthetic photon flux fluence rate or PPFFR (that is, photon scalar irradiance or scalar quantum irradiance, Smith and Wilson, 1972), which is defined as the integral of photon flux radiance at a point over all directions about the point. In other words, PPFFR is a measure of the total number of photons of PAR per unit time and area arriving at a point from all directions about the point when all directions are weighted evenly (Smith and Wilson, 1972). Such spherical,  $4\pi$  quantum sensors are now available commercially and respond equally

to all photons in the 400-700 nm range (units in  $\mu E \sec^{-1} m^{-2}$ ). Photosynthetic and phototropic responses of organisms are related to the number of quanta of light of specific frequencies (wavelengths) impinging upon biechemical receptor systems. The attenuation of illuminance under water between a spectral range of 350 to 700 nm is not exactly the same for energy units as it is for quanta (Steemann Nielsen and Willemoës, 1971; Lewis, 1975). The rate of attenuation of quanta is approximately equal to that of energy in moderately clear water bodies containing intermediate concentrations of dissolved organic carbon (approximately 5 mg  $l^{-1}$ ). In more transparent waters, energy is absorbed at a slower rate than quanta; the opposite is true in more deeply stained waters containing greater amounts of dissolved organic matter. Divergence in penetration of quanta and energy can increase in certain specific portions of the spectral range and thus affect the utilization by action spectra of organisms. For example, small differences in the utilization of illuminance during photosynthesis between diatoms, green algae, and blue-green algae with differing action spectra of photosynthetic pigments occur when the rate of illu-

<sup>\*</sup>The einstein has been used to represent both the quantity of energy in Avogadro's number of photons and also Avogadro's number of photons (Incoll, et al., 1977). When used as the quantity of photons, 1 einstein (E) = 1 mole =  $6.02 \times 10^{23}$  photons.

mination is measured in energy units. The ratio of total quanta to total irradiance energy within the spectral region of photosynthetic activity, however, varies by no more than  $\pm$  10 per cent and is 2.5  $\pm$  0.25  $\times$  10 $^{18}$  quanta  $\sec^{-1}$  watt $^{-1}$  within a number of waters differing in optical characteristics (Morel and Smith, 1974). The ratio can be used to determine accurately the total quanta available for photosynthesis from measurements of total energy; the converse is also true.

# Thermal Radiation in Lake Water

Lakewater behaves like a blackbody\* to radiation of low frequency (wavenumber <14,000 cm $^{-1}$ ) and long wavelengths (750 to >12,500 nm). Because of surface reflection, only about 97 per cent of thermal radiation is emitted into the atmosphere. The atmosphere does not function as a blackbody, but thermal radiation from it is influenced by water vapor pressure and the degree of cloud cover. At night, the net emission of thermal radiation from the surface of a lake, in cal cm $^{-2}$  day $^{-1}$ , approximates [11 · (°K of water - °K of air)] or simply [11 · (temperature of the water - that of the air)] (cf. discussion in Hutchinson, 1957).

#### **NET RADIATION**

The net amount of solar radiation affecting a lake can be referred to as the net radiation surplus  $(Q_B)$ :

$$Q_{\text{B}} = Q_{\text{S}} + Q_{\text{H}} + Q_{\text{A}} - Q_{\text{R}} - Q_{\text{U}} - Q_{\text{W}},$$

where:

Qs = direct solar radiation

 $Q_H$  = indirect scattered and reflected radiation from sky and clouds

Q<sub>A</sub> = long-wave thermal radiation from the atmosphere and from surrounding topography (the latter is usually insignificant)

 $Q_R$  = radiation reflected from the lake

 $Q_{\text{U}}$  = radiation scattered upward and lost  $Q_{\text{w}}$  = emission of long-wave radiation.

At night, most components are negligible, and the net radiation surplus becomes equal to the long-wave thermal radiation of the atmosphere minus that emitted from the water

$$Q_B = Q_A - Q_W$$

or, approximately,  $Q_B = -11$  (temperature of the water — the temperature of the air) in cal cm<sup>-2</sup> day<sup>-1</sup>. We will return to these relationships when discussing heat budgets in the following chapter. It should be emphasized, however, that even though the mean value of  $Q_B$  may be positive, the lake can be losing heat through evaporation and convective heating of the air (Hutchinson, 1957).

The collective value for the inputs  $(Q_s + Q_H + Q_A)$  can be measured directly by

<sup>\*</sup>A blackbody absorbs all of the radiant energy incident upon it. The thermal radiation (Q) from a blackbody is proportional to the fourth power of the absolute temperature (K).  $Q = 8.26 \times 10^{-9} (K)^4$ 

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sensitive Moll thermopile pyranometers. The subject of radiation measurement is treated excellently by Latimer (1972), Bickford and Dunn (1972), Šesták, Čatský, and Jarvis (1971), and Coulsen (1975).

### Transmission and Absorption of Light by Water

The quantity of light energy penetrating the water is dispersed by the mechanisms discussed above, and absorbed. The diminution of radiant energy with depth, by both scattering and absorption mechanisms, is referred to as light attenuation, whereas absorption is defined as diminution of light energy with depth by transformation to heat (cf. Westlake, 1965). It is important to understand the selective absorptive properties of water, first in pure water and then in lake waters of differing optical characteristics.

The transmission and absorption of light in water can be approached in several ways. Perhaps the most direct way is to look first at the percentage of transmission or absorption of monochromatic light through given depths of pure water. This percentile absorption, or Birgean percentile absorption (after E. A. Birge who used the relationship extensively), is based on the expression

$$\frac{100 \, (I_{0} - \, I_{z})}{I_{0}}$$

where

 $I_0$  = irradiance at the lake surface

 $I_z$  = irradiance at depth z, in this case taken as 1 m.

In distilled water, the percentile absorption is very high in the infrared region of the spectrum, decreases rapidly in the lower wavelengths to a minimum absorption in the blue, and then increases again in the violet and especially UV wavelengths (Table 5-2). These absorption relationships usually are expressed graphically in linear or, even better, in logarithmic form (Fig. 5-7). Generally about 53 per cent of the total light energy is transformed into heat in the first meter.

The light intensity or irradiance,  $I_z$ , at depth z is a function of intensity at the surface ( $I_0$ ) and the log of the negative extinction coefficient ( $\eta$ ) times the depth distance, z, in meters:

$$I_z = I_0 e^{-\eta z}$$
or  $lnI_0 - lnI_z = \eta z$ .

The extinction coefficient  $(\eta)$  is a constant for a given wavelength; approximate values for pure water are given in Table 5–2. This relationship is imperfect in nature because sunlight is not monochromatic, but is instead a composite of many wavelengths.

Direct sunlight rarely enters the water at right angles to the surface, and indirect irradiance is not perpendicular to the surface at any time. Moreover, the natural total extinction coefficient  $(\eta_t)$  is influenced not only by that of the water itself  $(\eta_w)$ , but also by absorption of particles suspended in the water  $(\eta_p)$ , and particularly by dissolved, colored compounds  $(\eta_c)$ . Thus the in situ extinction coefficient  $(\eta_t)$  is a composite of these components (Åberg and Rodhe, 1942):

$$\eta_{\rm t} = \eta_{\rm w} + \eta_{\rm p} + \eta_{\rm c}$$

TABLE 5-2 Absorption Coefficients (Percentile Absorption) and Extinction Coefficients of Monochromatic Light of Liquid Water at 21.5°C by Laser Optoacoustic Spectroscopy\*

WAVELENGTH (nm)	WAVE NUMBER (v¹) (cm⁻¹)	ABSORPTION COEFFICIENT (10 <sup>-4</sup> cm <sup>-1</sup> ) ("PERCENTILE ABSORPTION")	EXTINCTION COEFFICIENT (η m <sup>-1</sup> )	
820 (infrared)	12,200	(91.1)		
800 `	12,500	(89.4)	2.24	
780	12,820	(90.1)	2.31	
760	13,160	(91.4	2.45	
740	13,515	(88.5)	2.16	
720	13,890	(64.5)	1.04	
700	14,285	59.0	0.89	
689.2	14,500	47.6	0.646	
680.1 (red)	14,700	42.6	0.555	
666.5	15,000	38.7	0.489	
645.0	15,500	31.4	0.377	
624.8 (orange)	16,000	29.6	0.351	
605.9	16,500	24.8	0.285	
588.0	17,000	12.3	0.131	
574.5 (yellow)	17,400	8.1	0.084	
546.3	18,300	5.3	0.054	
526.2 (green)	19,000	4.0	0.041	
512.7	19,500	3.48	0.0354	
499.9	20,000	2.33	0.0236	
487.7	20,500	1.86	0.0188	
473.1	21,000	1.79	0.0181	
465.0 (blue)	21,500	2.06	0.0208	
454.4	22,000	2.21	0.0224	
446.3	22,400	2.38	0.0241	

\*For data from 700 to 446 nm (Tam and Patel, 1979). Values in parentheses are older data determined by 1-meter path transmission measurements from James with Birge (1938).

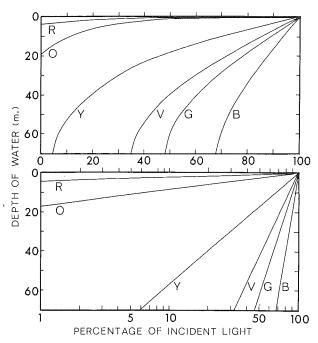


Figure 5-7 Transmission of light by distilled water at six wavelengths (R-720, O-620, Y-560, G-510, B-460, V-390 nm). Percentage of incident light that would remain after passing through the indicated depths of water expressed on a linear (upper) and a logarithmic (lower) scale. (After Clark, 1939.)

At low concentrations, the particulate suspensoids have relatively little effect on absorption. With high turbidity, however, the effect is quite significant, particularly at lower wavelengths of the visible spectrum. In detailed analyses of the absorption of lake water and its dissolved components, the particulate fraction is commonly removed by filtration or centrifugation.

#### EFFECTS OF ORGANIC COMPOUNDS

The effects of dissolved organic compounds on the absorption of light energy are very marked, and are best introduced by examples taken from the extensive work of James with Birge (1938). In comparison to distilled water, lake water with increasing concentrations of dissolved organic compounds, particularly humic acids, not only drastically reduces the transmission of light, but shifts the absorption selectively (Table 5–3). Common to all waters is a very high absorption of infrared and red wavelengths, which results in significant heating effects in the first meter of water. At the other extreme, while distilled water absorbs relatively little UV light, even very low concentrations of dissolved organic compounds increase UV absorption greatly. In lakes highly stained with humic compounds, such as Helmet Lake, absorption of UV, blue,

TABLE 5-3 Percentile Absorption of Light of Different Wavelengths by One Meter of Lake Water, Settled of Particulate Matter, of Several Wisconsin Lakes of Progressively Greater Concentrations of Organic Color\*

WAVELENGTH (nm)	DISTILLED WATER	CRYSTAL LAKE	LAKE MENDOTA	ALELAIDE LAKE	MARY LAKE	HELMET LAKE
800	88.9	89.9	90.5	92.4	91.7	93.2
780	90.2	91.3	91.9	93.5	93.0	94.5
760	91.4	93.5	92.6	94.5	94.8	96.0
740	88.5	89.3	91.5	92.7	93.0	96.2
720	64.5	67.6	71.0	78.0	78.0	86.9
700	45.0	50.4	49.7	66.3	70.7	82.5
685	38.0	45.2	42.2	65.7	$\tilde{7}1.7$	86.6
668	33.0	40.3	36.8	65.0	72.3	88.0
648	28.0	37.0	31.9	64.5	75.2	91.2
630	25.0	34.4	28.9	65.8	77.8	94.0
612.5	22.4	32.1	26.3	66.8	80.3	96.0
59 <i>7</i>	17.8	27.5	22.5	67.0	83.2	97.6
584	9.8	22.0	17.6	67.1	85. <i>7</i>	98.2
568.5	6.0	19.3	14.0	67.6	88.5	98.6
546	4.0	19.2	13.5	70.9	91.6	99.3
525	3.0	19.8	14.1	74.5	94.8	_
504	1.1	20.7	15.2	81.0	97.4	_
473	1.5	21.7	21.7	88.6	99.4	_
448	1.7	23.8	27.8	92.2		_
435.9	1.7	24.4	31.0	95.2	_	-
407.8	2.1	28.1	44.3	99.0	_	_
365	3.6	40.0	80.0	-	-	-
Color Scale (Pt units)	0	0	6	28	101	264

<sup>\*</sup>Selected data from James and Birge, 1938.

and green wavelengths is essentially complete in much less than a depth of 1 meter. This relationship of intense absorption of UV light by dissolved organic compounds has been used extensively as a relative assay of their concentrations, as will be discussed in a subsequent chapter on organic matter.

The major effects of dissolved organic matter and particulate suspensoids on absorption of light at varying wavelengths are illustrated graphically in Figure 5-8. The

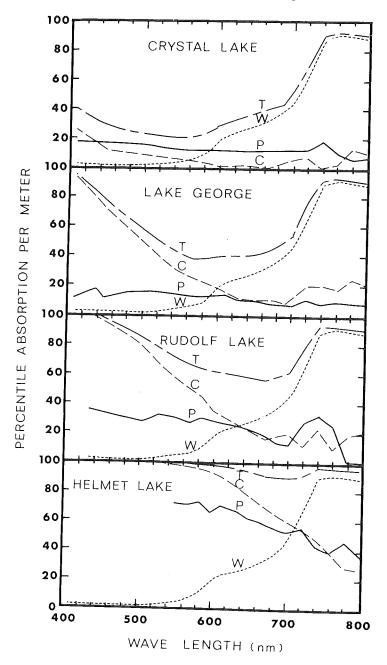


Figure 5-8 Percentile absorption of light at different wavelengths passing through 1 meter of water of 4 lakes of northern Wisconsin of increasing concentrations of dissolved organic matter. T = total absorption; C = absorption by dissolved organic color; P = absorption by suspended particulate matter; and W = absorption by pure water. (Modified from James and Birge, 1938.)

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ds on 3. The total absorption characteristics in the spectrum (T) are compared to the percentile absorption values through 1 meter of distilled water (W), absorption attributable to particulate suspensoids (P), and absorption by lake water that has been filtered to remove particles  $>1~\mu m$  (C), termed color absorption. Absorption by dissolved organic compounds ("dissolved color") is selective and greatest in the UV, blue, and green wavelengths. The absorption by dissolved color at the red end of the spectrum is less selective, and is probably unrelated to the organic compounds absorbing at lower wavelengths. The extinction coeffcients of dissolved color ( $\eta_c$ ) increase directly with the color units of the water, which are measured by the relative visual comparisons of the color of the filtered lake water under standard conditions to the color of a specific mixture of platinum-cobalt compounds in serial dilution (discussed further on). In the examples given in Figure 5–8, the water of Crystal Lake indicated zero platinum (Pt) units, Lake George, 24, Rudolf Lake, 50, and that of Helmet Lake, 236 Pt units, which is about the color of weak tea.

Also apparent from this classic work is the relationship that absorption resulting from particulate suspensoids (P) is relatively unselective at different wavelengths, particularly at lower concentrations. The  $\eta_p$  functions essentially independently of the  $\eta_c$  but, along with the absorption of water  $(\eta_w)$ ,  $\eta_p$  values are additive for a particular lake at depth at a given time of year (cf. Åberg and Rodhe, 1942).

### ANALYSIS OF LIGHT TRANSMISSION

The transmission or absorption within a lake of the total white light from direct insolation and indirectly from the sky has been analyzed in many ways. The vertical extinction coefficient is most commonly determined from the percentile absorption of surface light through depth (Fig. 5–9). The isopleths\* of these examples of depth-time distribution of light indicate some of the marked fluctuations that are found in natural waters, seasonally and vertically. The composite mean  $\eta_t$  of all depths in Lawrence Lake, an unproductive hard-water lake with rather high concentrations of particulate and colloidal CaCO<sub>3</sub> suspensoids, was  $0.39~\text{m}^{-1}$  (n = 1,746), within an annual range of 0.05 to 1.02. The same value for extremely productive Wintergreen Lake was 1.00 m<sup>-1</sup> (range 0.46 to 1.68). In the former case, the  $\eta_t$  is largely constant over an annual period, whereas in the latter situation the marked fluctuations in particulate suspensoids of algae are reflected in the mean  $\eta_t$  m<sup>-1</sup> and mean percentage transmission m<sup>-1</sup> of the water column (Fig. 5–10).

Calculations of the vertical extinction coefficient are not very reliable in the first meter below the surface because of surface agitation. Average calculations often exclude this region. Direct calculations are made using the formula given earlier, or changed to

$$\eta z = \ln I_0 - \ln I_z$$

A nomogram for estimating the extinction coefficient directly from light transmission data is given in the appendices.

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<sup>\*</sup>An isopleth is a line on a graph of a specified constant value showing the occurrence of a parameter as a function of two variables (depth and time in this case). See Wetzel and Likens (1979:26) for details of preparation of these diagrams.